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by

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Described will be an improved monomer synthesis for planar polyphenylene derivatives. A retrosynthetic approach is shown below. Both monomers come from a common arylbis(acid chloride).

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Improved Route to Bridged Planar Poly(*p*-phenylene) Derivatives for Maximization of Extended π-Conjugation

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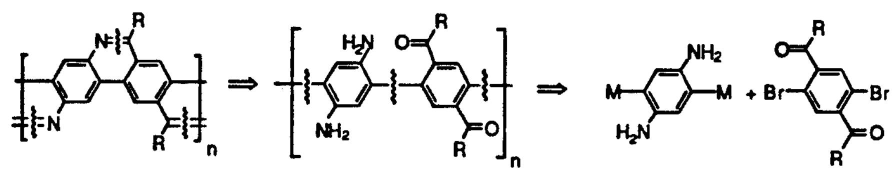
Poly(*p*-phenylene) (PPP), a highly insoluble polymer that has been studied extensively for its possible electronic and photonic applications, has a 23° twist between the consecutive aryl units due to ortho hydrogen interactions.[1] Attempts to enhance the solubility by substitution of the rings forces the consecutive aryl units even further out of plane resulting in a plummet of the extended conjugation (easily observed by the optical spectra).[1] We recently described a route to soluble ladder PPP derivatives.[2] Here we describe an improved synthetic route to the monomers as well as an aryl-substituted ladder PPP derivative.[3]

Our retrosynthetic approach involved two key steps (Scheme I, M = metal). First, imine cleavage to the

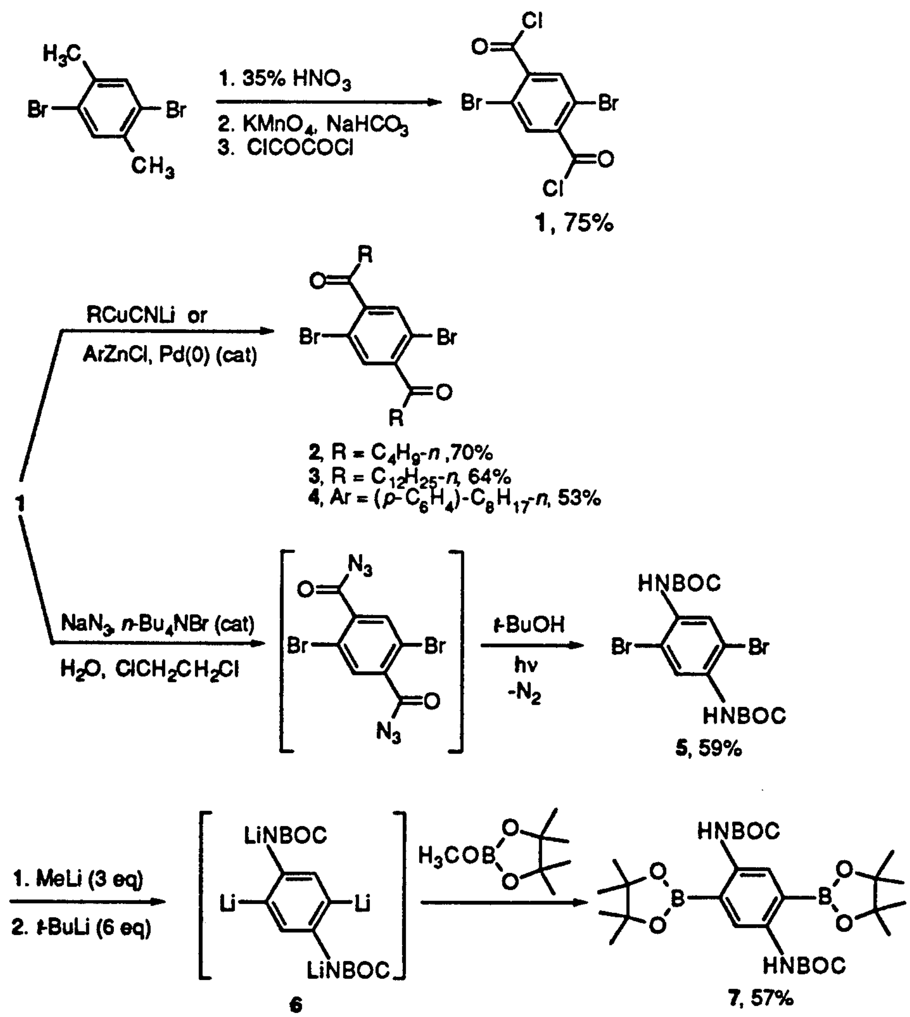
Scheme I



ketoamine functionalized PPP, and second, bond cleavage to the two arene systems shown. Since Pd(0)-catalyzed oxidative addition reactions are facilitated with electron deficient ring systems,[4] we chose to keep the halides on the ketoaromatic portion.

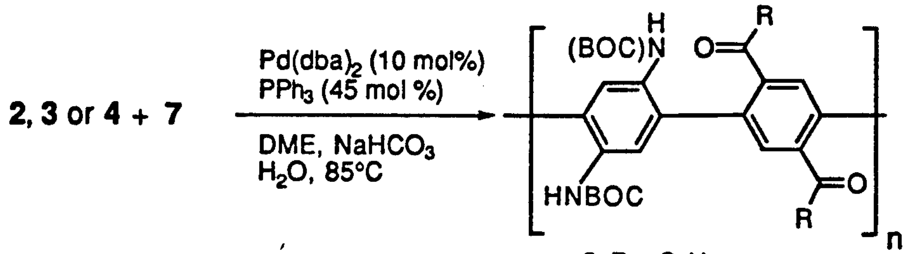
After several nearly quantitative model reactions, we synthesized the two key monomers needed for the desired AB-type step growth polymerization. Dibromoxylene was oxidized by a two-step procedure[5] which was superior to the one step $Co(OAc)_2$ procedure[2] described previously. The route described here is an improvement over our former approach in that the same dibromobis(acid chloride) (**1**) can be used for the synthesis of both the A and B monomer units. Conversion of **1** to the diketone was

accomplished with the use of the lower order alkylcyanocuprate, or an arylzinc halide and Pd(0) catalysis.[6] This Pd(0)-catalyzed procedure proved to be superior for the aryl ketone formation. **1** could also be converted to the bis(acylazide) under phase transfer conditions. Photolysis with a UV TLC-spotting light affected the bis-Curtius rearrangement with N_2 expulsion. *t*-BuOH trapping of the bis(isocyanate) afforded the desired bis(BOC)-protected amine **5**.[7] These phase transfer conditions and subsequent photochemical rearrangements were the only set of conditions that worked, in our studies, for this transformation. The yield of 59% for **5** is after repeated crystallization, thus, the efficiency of this process is quite good.

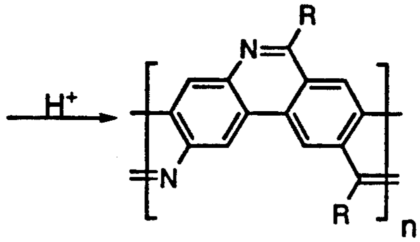


While **5** was nearly insoluble in ether at 0°C, it could be tetralithiated in ether to form a soluble intermediate **6** in almost quantitative yield (checked by addition of TMSCl and isolation of the arylbis(silane) after aqueous work-up). Treatment of **6** with methyl pinacol borate afforded the monomer **7** which could be purified by passage through a flash chromatography column containing a mixture of activated charcoal and Celite as the stationary phase (silica gel or neutral alumina caused rapid decomposition of the intermediate) and CH_2Cl_2 as the eluant followed by recrystallized to form pure **7**.

Reaction of **2**, **3**, or **4** with **7**, in the presence of a Pd(0) catalyst, yielded the soluble polymers **8**, **9**, and **10**, respectively, from which size exclusion chromatography (SEC) could be used to determine the hydrodynamic volumes relative to polystyrene (**8**: 63% yield after fractional precipitation, M_n = 9,850 with M_w/M_n = 1.85; **9**: 97% yield after fractional precipitation, M_n = 28,400 with M_w/M_n = 3.70; **10**: 80% yield after fractional precipitation, M_n = 18,500 with M_w/M_n = 2.75). Upon exposure of **8**, **9**, or **10** to trifluoroacetic acid (TFA), quantitative loss of the BOC protecting group and cyclization afforded **11** (90% yield), **12** (97% yield), and **13** (90% yield), respectively.[8] All stretches for the ketone, carbamate, and amine in **8**, **9**, and **10** were absent in the FTIR spectrum of the planar polymers.



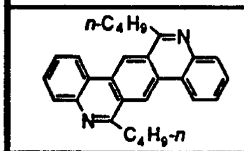
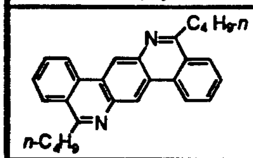
8, R = C_4H_9-*n*
9, R = $C_{12}H_{25}$-*n*
10, Ar = (*p*-C_6H_4)-C_8H_{17}-*n*



11, R = C_4H_9-*n*
12, R = $C_{12}H_{25}$-*n*
13, Ar = (*p*-C_6H_4)-C_8H_{17}-*n*

The optical absorption data showing enormous bathochromic shifts in the polymers upon cyclization (conversion of **8** to **11**, **9** to **12**, and **10** to **13**); an observation consistent with the proposed ladder formation (Table I). The UV-vis spectrum of **13** in a CH_2Cl_2/trifluoroacetic acid (3/2) mixture is shown in Figure 1. The absorptions of these planar polymers are far more bathochromically-shifted than those of the planar trimers,[9] oligo(*p*-phenylenes), and PPP.[10]

Table I. Optical Absorption Data

Compound	λ in solution (nm)[a]	λ of solid (nm)[a]
8	CH_2Cl_2: 250, 306 (sh)	248, 308[b]
9	CH_2Cl_2: 250, 388	250, 398[b]
10	CH_2Cl_2: 254	254
11	CH_2Cl_2/TFA: 374, 396, 426 (sh), 514, 520 (ed)[c]	------
12	CH_2Cl_2/TFA: 376, 400, 428, 478, 516, 530 (ed)[c]	463-490[d]
13	CH_2Cl_2/TFA:380, 402, 458, 506, 549[c]	-------
	CH_2Cl_2: 300 (ref 9)	------
	CH_2Cl_2: 294 (ref 9)	------
p-sexiphenylene	$CHCl_3$: 318 (ref 10)	------
PPP (calcd infinite M_n)	344 (ref 10)	------

[a]λ_{max} is underlined, (sh) is shoulder, (ed) is tailing edge at ~10% of λ_{max} intensity. [b]Also a strong carbonyl absorption at 196 nm. [c]Spectrum recorded on the acid solublized, therefore, multiprotonated system. [d]These λ_{max} values were recorded on a series of four different polymer samples of **9** in order to insure their reproduciblity.[11]

Figure 1. UV-vis spectrum of **13** in a CH_2Cl_2/TFA (3/2) mixture

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(7) We developed these rearrangements conditions at the same time that Swager described an analogous procedure without BOC protection. See: Zhou, Q.; Swager, T. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*(1), 277. Our development was based on work by Pfister. See: Pfister, J. R.; Wymann, W. E. *Synthesis* **1983**, 38.

(8) **8**: Anal. calc'd for $(C_{32}H_{42}N_2O_6)_n$: C, 69.79; H, 7.69; N, 5.07. Found: C, 70.55; H, 7.25; Br, <0.5; N, 5.13. **9**: Anal. calc'd for $(C_{48}H_{74}N_2O_6)_n$: C, 74.38; H, 9.62; N, 3.61. Found: C, 74.99; H, 9.40; Br, <0.5; N, 3.55. **11**: Anal. calc'd for $(C_{22}H_{22}N_2)_n$: C, 84.04; H, 7.05; N, 8.91. Found: C, 79.13; H, 6.77; Br, <0.5; N, 8.56. **12**: Anal. calc'd for $(C_{38}H_{54}N_2)_n$: C, 84.70; H, 10.10; N, 5.20. Found: C, 81.45; H, 9.64; Br, <0.5; N, 5.22.

(9) The planar trimers were prepared during our model studies for the polymerizations described here using Pd-catalyzed couplings.

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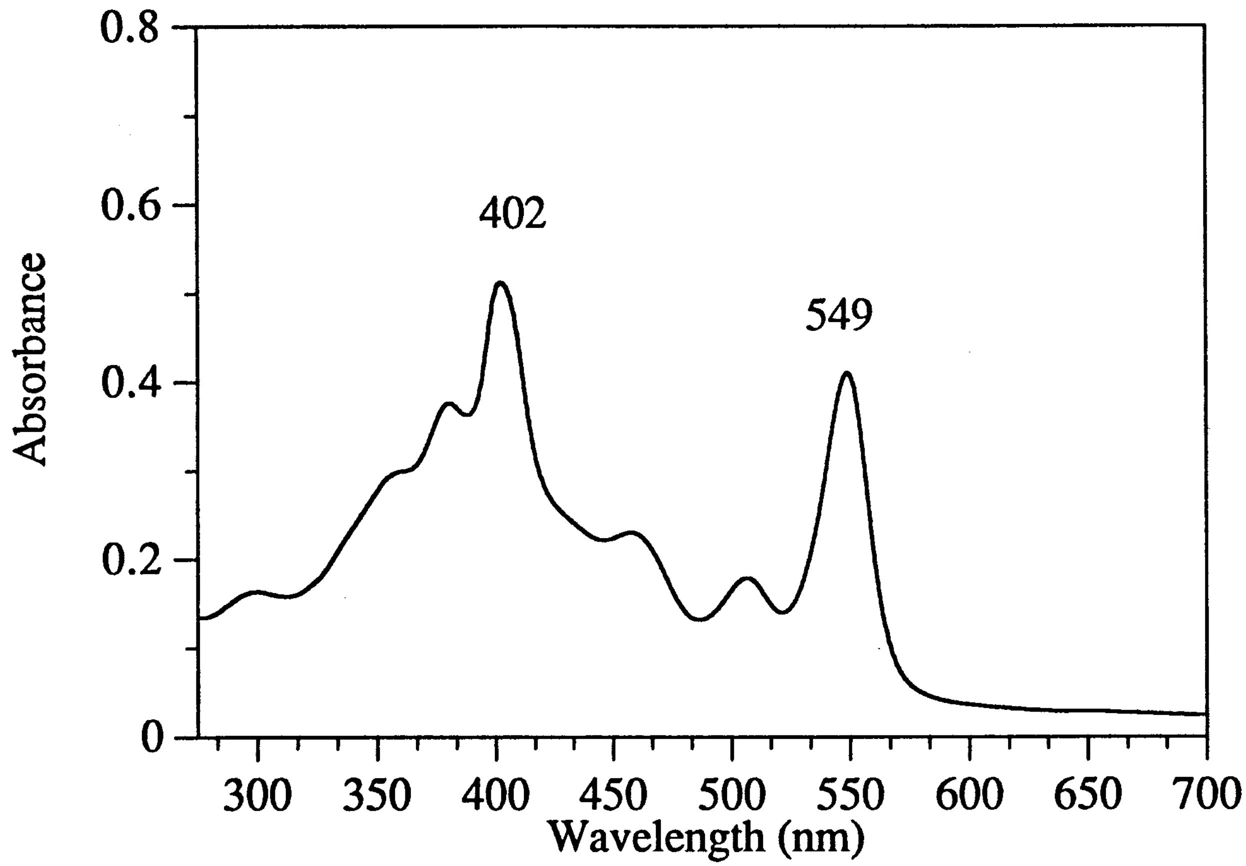
(11) Drs. R. Gaudiana and P. Mehta of Polaroid Corporation kindly provided the solid-state UV-vis data.


0.8
0.6
0.4
0.2
0
Absorbance
402
549
300
350
400
450
500
550
600
650
700
Wavelength (nm)